Pilot Plant Performance and Process Simulation of a Hydrophobic Physical Solvent for Pre-combustion CO_2 Capture

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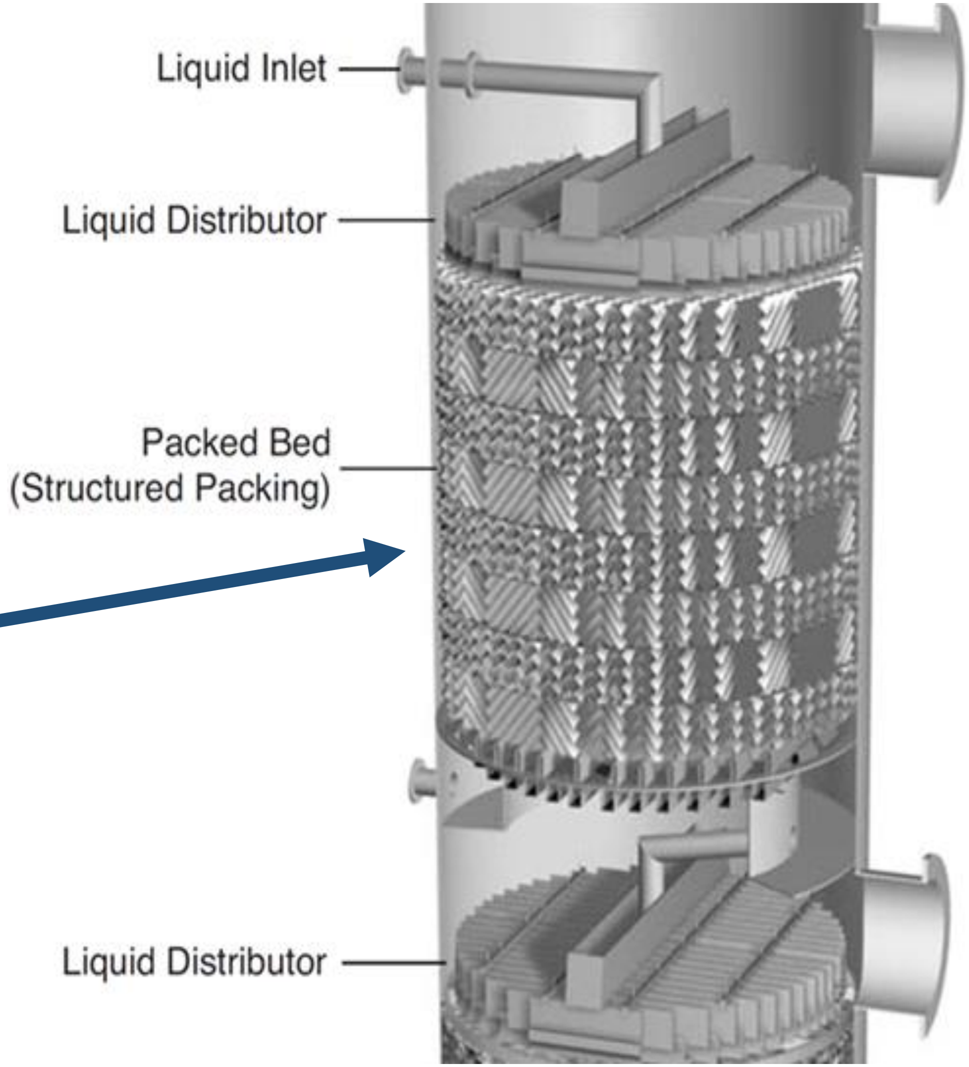
NATIONAL ENERGY TECHNOLOGY LABORATORY

Applications for Physical Solvents for Gas Separation

Tailored markets: [Blue Hydrogen]

- Pre-combustion CO_2 Capture at IGCC-CCS
- Generation of H_2 from SMR-CCS

Polygeneration of fuels, fertilizers, & chemicals



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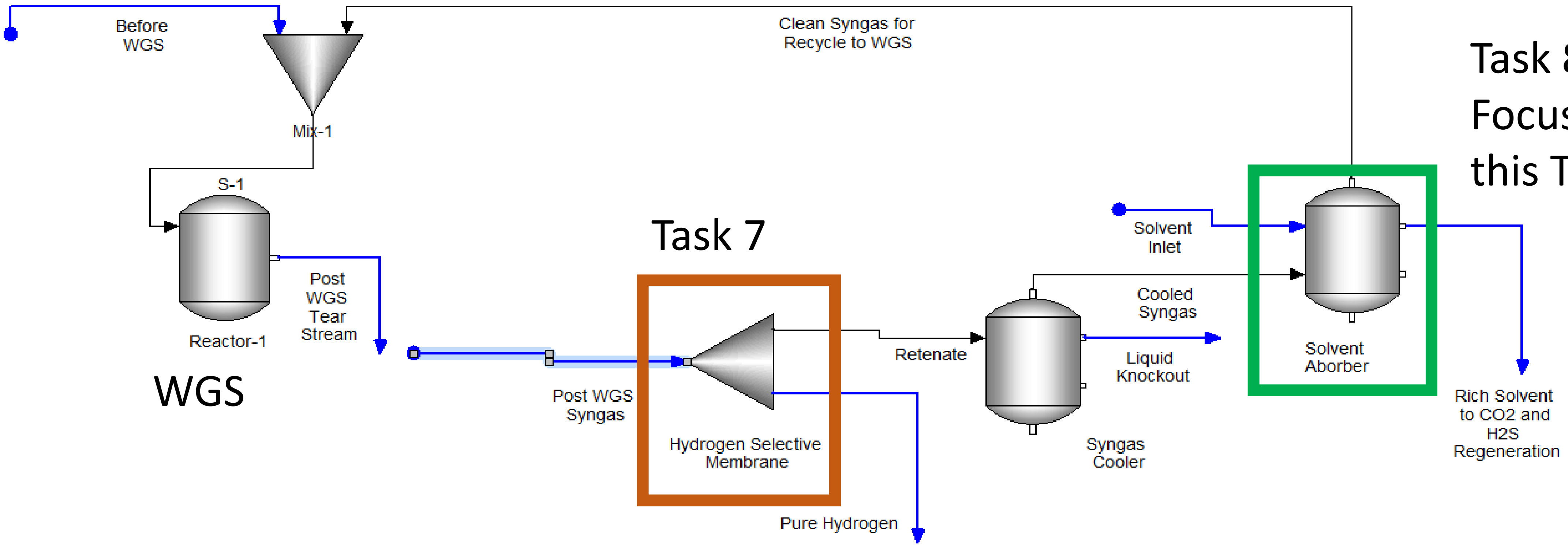
Hybrid Precombustion Capture for Flexible Operations

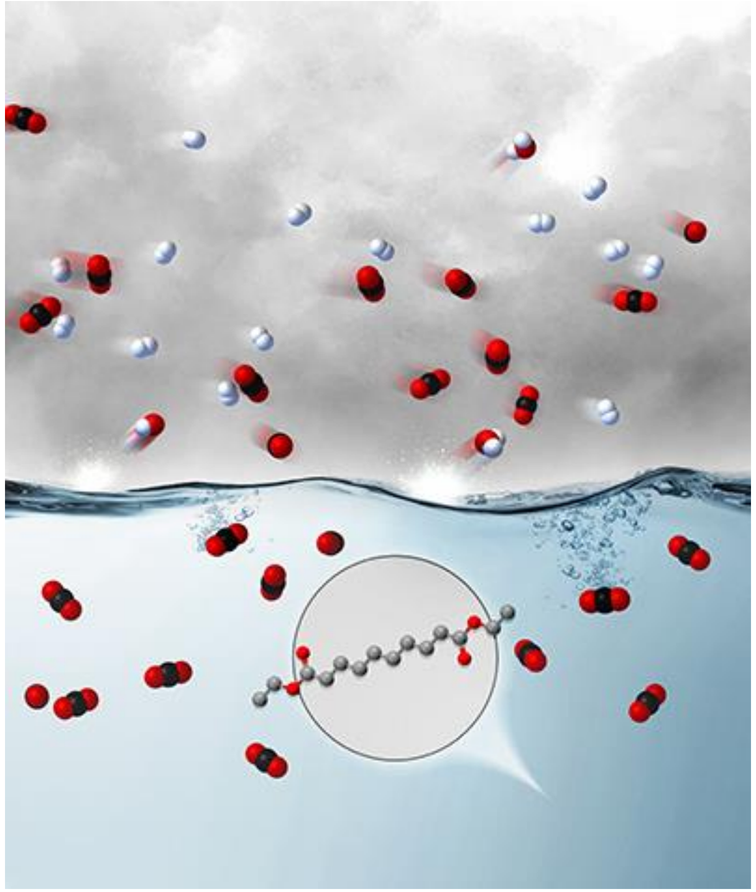
- **Upstream H_2 selective membrane (Task 7)**
- **CO_2 selective solvent (Task 8)**



Task 8: Focus of this Talk

Physical Solvents for Pre-combustion CO_2 Capture

4 physical solvents were tested for pre-combustion CO_2 capture performance at bench scale and pilot plant scale: **1 hydrophilic solvent PEGDME (Selexol Surrogate)**
3 hydrophobic solvents: PEG-PDMS-3, CASSH-1, TBP



Solvent	**PEGDME**	**CASSH-1**	**PEG-PDMS-3**	**TBP**
Molecular Weight ($g \cdot mol^{-1}$)	280	258	620	266
Viscosity @ 25 ℃ (cP)	5.8	5.1	12.2	2.9
Density @ 25 ℃ ($kg \cdot m^{-3}$)	1030	960	987	979
Vapor pressure @ 25°C (Pa)	0.1	0.07	<0.1	0.15

Shi, W. et al. 2021. Computational Screening of Physical Solvents for CO_2 Pre-combustion Capture. The Journal of Physical Chemistry B 125, 13467-13481.
Shi, W. et al. 2019. Molecular Simulations of CO_2 and H_2 Solubility, CO_2 Diffusivity, and Solvent Viscosity at 298 K for 27 Commercially Available Physical Solvents. Journal of Chemical & Engineering Data 64, 3682-3692.

From Lab to Pilot Plant to Process Simulation

Bench scale

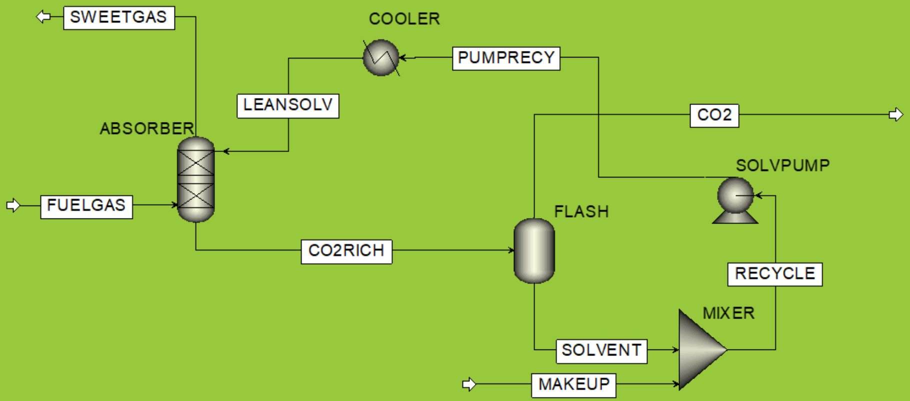
- CSTR, Hiden & Isosorp
- Pure gas vapor liquid equilibrium (VLE) measurements for CO_2, H_2, N_2, CH_4

Pilot plant scale

- UND EERC
- Multi-component coal syngas
- Solvent screening
- Long term solvent testing

Process simulation

- Aspen Plus incorporates bench-scale VLE data
- Predicts pilot plant performance
- Compare results with pilot plant exp. data



Performance of hydrophobic physical solvents for pre-combustion CO_2 capture at a pilot scale coal gasification facility

Kathryn H. Smith, Husain E. Ashkanani, Robert L. Thompson, Jeffrey T. Culp, Lei Hong, Mike Swanson, Joshua Stanislowski, Wei Shi, Badie I. Morsi, Kevin Resnik, David P. Hopkinson, Nicholas S. Siefert*, *Unpublished*.

Bench Scale VLE Measurements

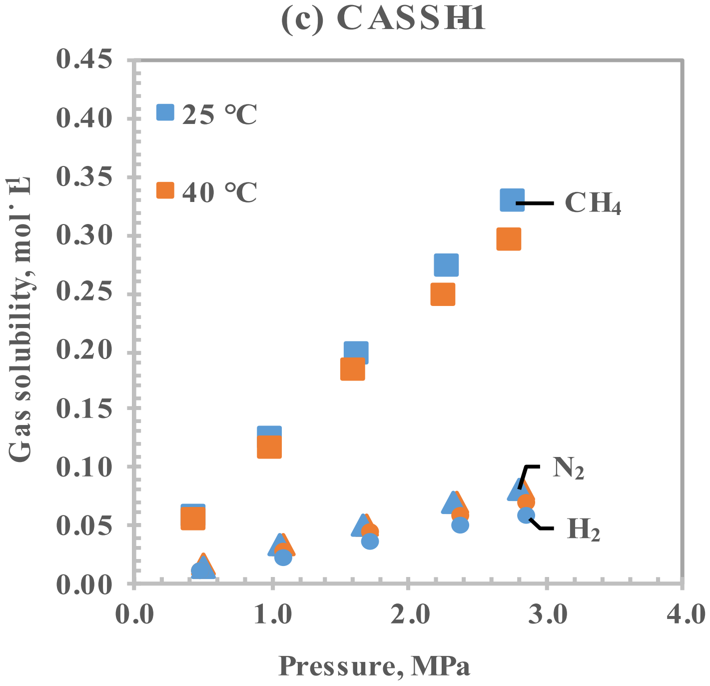
$$\text{Gas solubility}\left(\frac{mol}{L}\right) = \frac{\text{gas absorbed into solvent (mol)}}{\text{Lean solvent volume (L)}}$$

@ specific temperature, partial pressure

$$\text{Selectivity A/B} = \frac{\text{Gas solubility } gas\ A\ (mol\ L^{-1})}{\text{Gas solubility } gas\ B (mol\ L^{-1})}$$

@ specific temperature, same partial pressures

- CSTR
- Hiden IGA system
- Rubotherm IsoSorp (TA Instruments)

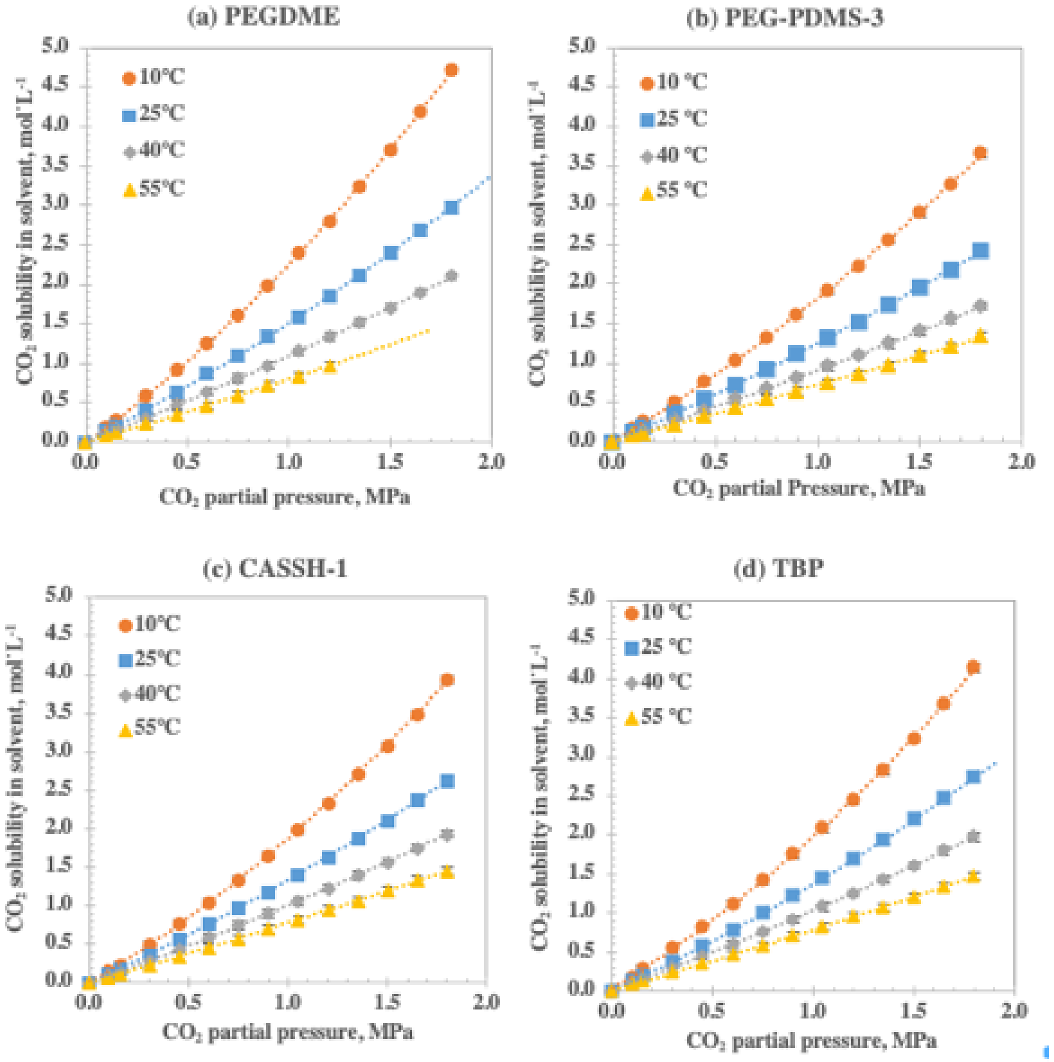


Selectivity A/B @ 25℃, 1 MPa, pure gas

Solvent	PEGDME	CASSH-1	PEG-PDMS-3	TBP
CO_2/H_2 Selectivity	71	51	48	40
CO_2/N_2 Selectivity	71	36	38	34
CO_2/CH_4 Selectivity	15	8	8	8

Vapor Liquid Equilibrium Results

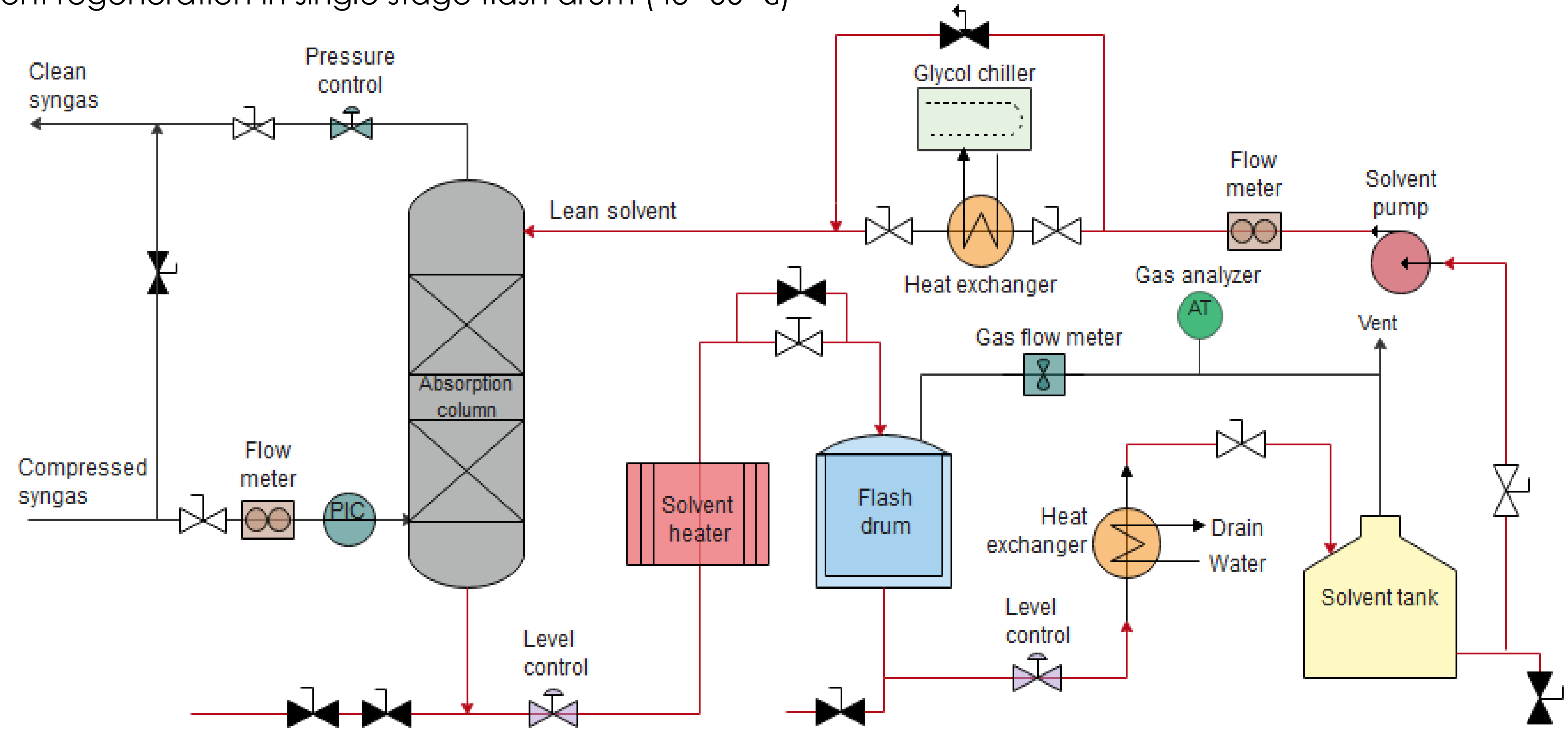
- Solubility of CO_2 increases with increasing pressure and decreases with increasing temperature
- PEGDME shows slightly higher CO_2 uptake at 10 °C and 25°C, however, as the solvent temperature increases, the CO_2 solubility in PEGDME decreases at a faster rate than the hydrophobic solvents



Temperature	CO_2 solubility at 1 MPa (mol×L^{-1})			
	PEGDME	CASSH-1	PEG-PDMS-3	TBP
10°C	2.26 ± 0.042	1.88 ± 0.042	1.82 ± 0.015	1.97 ± 0.019
25°C	1.50 ± 0.019	1.34 ± 0.020	1.25 ± 0.007	1.37 ± 0.013
40°C	1.10 ± 0.007	1.01 ± 0.007	0.906 ± 0.003	1.03 ± 0.004
55°C	0.80 ± 0.007	0.78 ± 0.005	0.718 ± 0.003	0.78 ± 0.003

UND EERC Pilot Plant - Process Flow Diagram

Absorber: 76.2 mm ID, 3.2 m packed height (5/8 ” IMTP15 metal random packing)
Solvent regeneration in single stage flash drum (43 -66 °C)



UND EERC Pilot Plant – Operating Conditions

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Solvent operating conditions for each trial

	Trial 1 - Screening (~5 hrs per case)	Trial 2 – long term (5 days per case)
Solvents	Selexol (PEGDME) CASSH-1 PEG-PDMS-3 TBP	Selexol (PEGDME) CASSH-1
Temperature (lean solvent)	10, 25, 40, 55 °C	25 °C
Solvent flow rate	28 - 45 L/h	32 L/h
Solvent regeneration temperature	43 °C	66 °C

Average syngas conditions & composition for each trial

Parameter	Trial 1	Trial 2
Syngas total pressure, MPa	4.88 ± 0.02	4.86 ± 0.01
Syngas temperature, °C	37.5 ± 0.8	37.6 ± 0.4
Syngas flow rate, std. $m^3 \cdot h^{-1}$	3.8 ± 0.2	3.5 ± 0.1
Syngas composition, avg dry, mol%		
CO_2	52.0 ± 1.8	55.4 ± 1.5
H_2	13.1 ± 2.9	15.7 ± 1.3
N_2	32.7 ± 3.7	25.4 ± 2.1
CH_4	1.6 ± 0.7	2.1 ± 0.32
CO	0.2 ± 0.05	1.1 ± 0.39
H_2S	0.5 ± 0.05	0.4 ± 0.05

$$\mathrm{CO_2\ Removal\ Efficiency\ [\%]} = \frac{\mathrm{CO_2\ absorbed\ into\ solvent\ (mol \cdot hr^{-1})}}{\mathrm{CO_2\ in\ syngas\ (mol \cdot hr^{-1})}} \times 100$$

L/V Trial#2 = 6.7

$$\mathrm{Gas\ Uptake\ into\ solvent\ [mol\ L^{-1}]} = \frac{\mathrm{CO_2\ absorbed\ in\ solvent\ (mol \cdot hr^{-1})}}{\mathrm{Solvent\ flow\ rate\ (L \cdot hr^{-1})}}$$

Pilot Plant Trial 1 – Solvent Screening Results

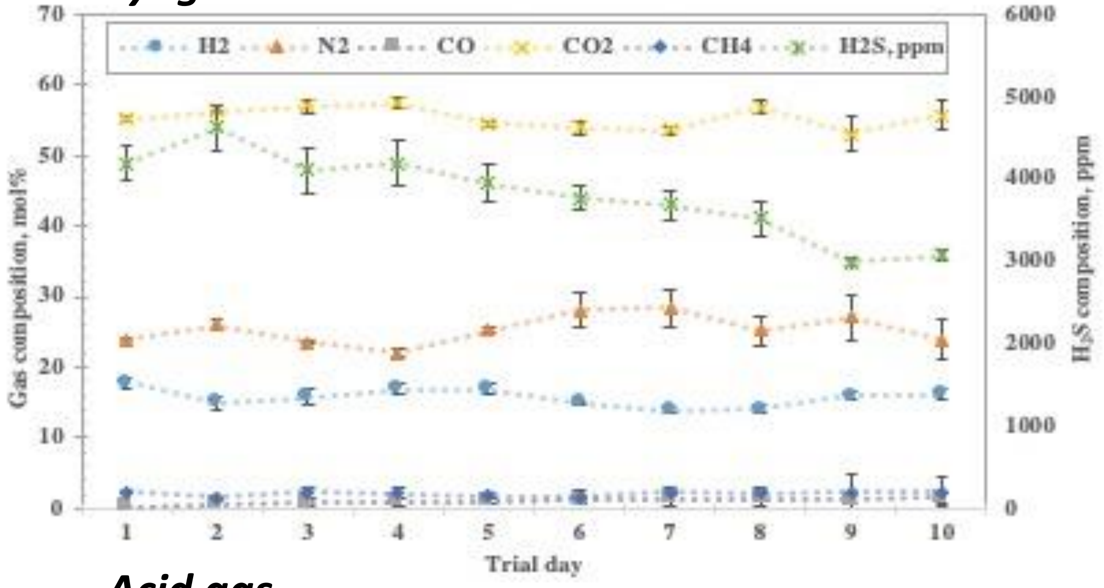
- Four different physical solvents and varying operating conditions including temperature and solvent flow rate (~5 hrs per condition)
- All solvents were operated at similar operating conditions and showed comparable CO_2 absorption performance
- Hydrophobic solvents showed comparable or higher CO_2 and H_2S absorption performance, including at elevated solvent temperatures
- Hydrophobic solvents contained less water at end of testing period

Solvent Temp*	Performance parameter	Hydrophilic PEGDME	Hydrophobic PEG-PDMS-3	Hydrophobic CASSH-1	Hydrophobic TBP
10°C	Solvent temp inlet – outlet, °C	10.1 – 13.8	9.5 – 20.5	10.4 – 28.5	10.7 – 13.9
	CO_2 gas uptake, mol L^{-1}	1.64 ± 0.10	1.72 ± 0.10	2.27 ± 0.03	1.50 ± 0.06
	H_2S gas uptake, mol L^{-1}	0.014 ± 0.001	0.014 ± 0.001	0.021 ± 0.001	0.015 ± 0.001
25°C	Solvent temp inlet – outlet, °C	25.0 – 27.0	25.3 – 33.6	25.6 – 32.6	25.1 – 26.8
	CO_2 gas uptake, mol L^{-1}	1.46 ± 0.14	1.63 ± 0.02	1.66 ± 0.04	1.65 ± 0.04
	H_2S gas uptake, mol L^{-1}	0.011 ± 0.001	0.012 ± 0.001	0.015 ± 0.001	0.016 ± 0.001
40°C	Solvent temp inlet – outlet, °C	**	40.0 – 46.6	40.6 – 48.0	39.8 – 41.4
	CO_2 gas uptake, mol L^{-1}	**	1.64 ± 0.07	1.91 ± 0.05	1.90 ± 0.01
	H_2S gas uptake, mol L^{-1}	**	0.014 ± 0.001	0.018 ± 0.001	0.018 ± 0.001
55°C	Solvent temp inlet – outlet, °C	**	54.3 – 63.7	55.4 – 57.4	55.5 – 58.5
	CO_2 gas uptake, mol L^{-1}	**	1.55 ± 0.10	1.67 ± 0.05	1.92 ± 0.01
	H_2S gas uptake, mol L^{-1}	**	0.014 ± 0.001	0.016 ± 0.001	0.018 ± 0.001
Water content of solvent at end of trial, ppm		4000*	550	1550	1670

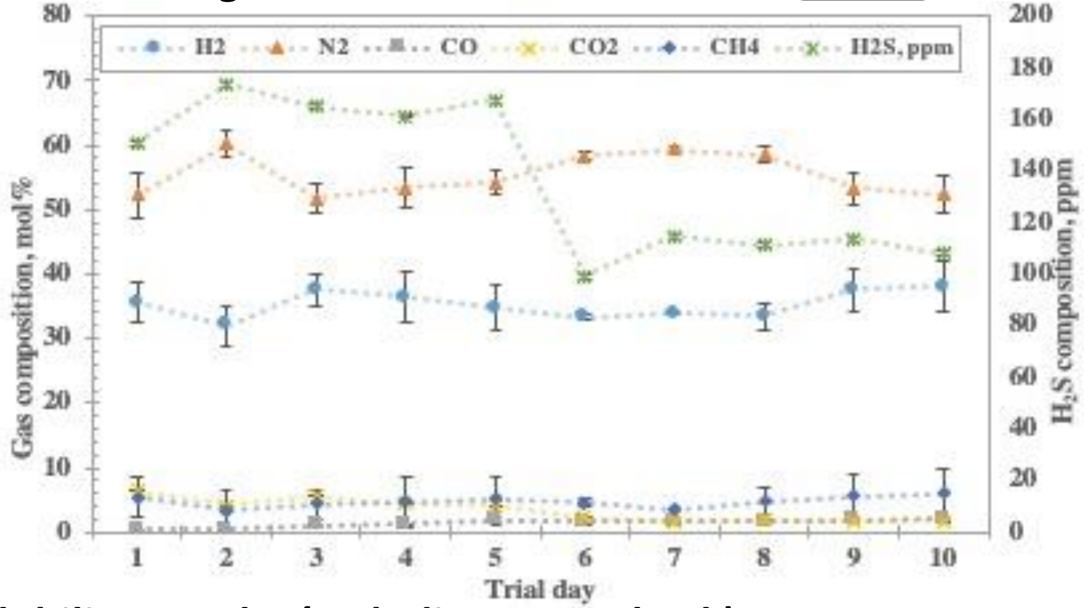
*=PEGDME was not operated at 55°C so water content measured after 43°C flash

Pilot Plant Trial 2 – Longer Term Testing

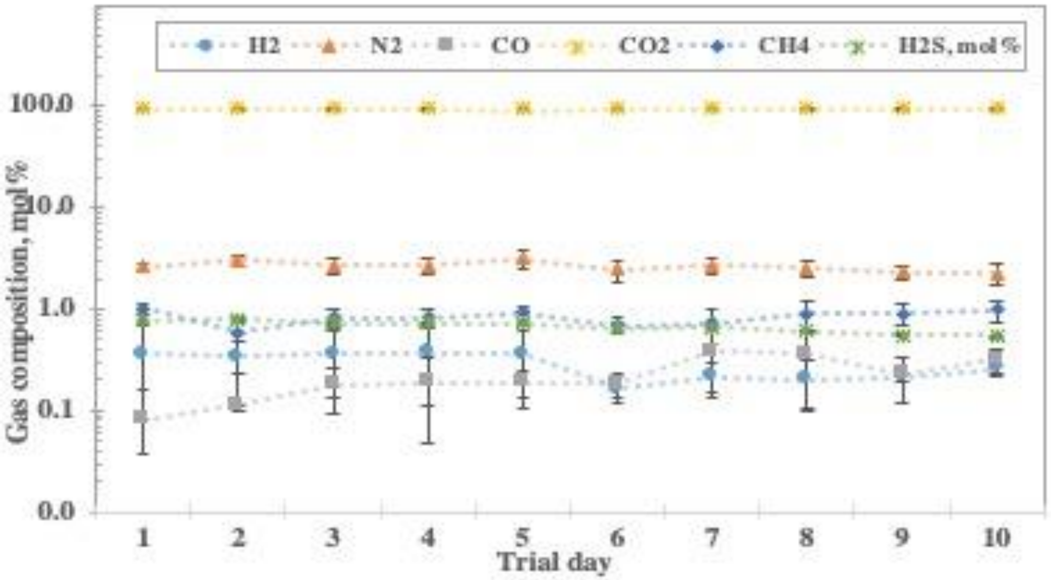
Syngas



Sweet gas



Acid gas



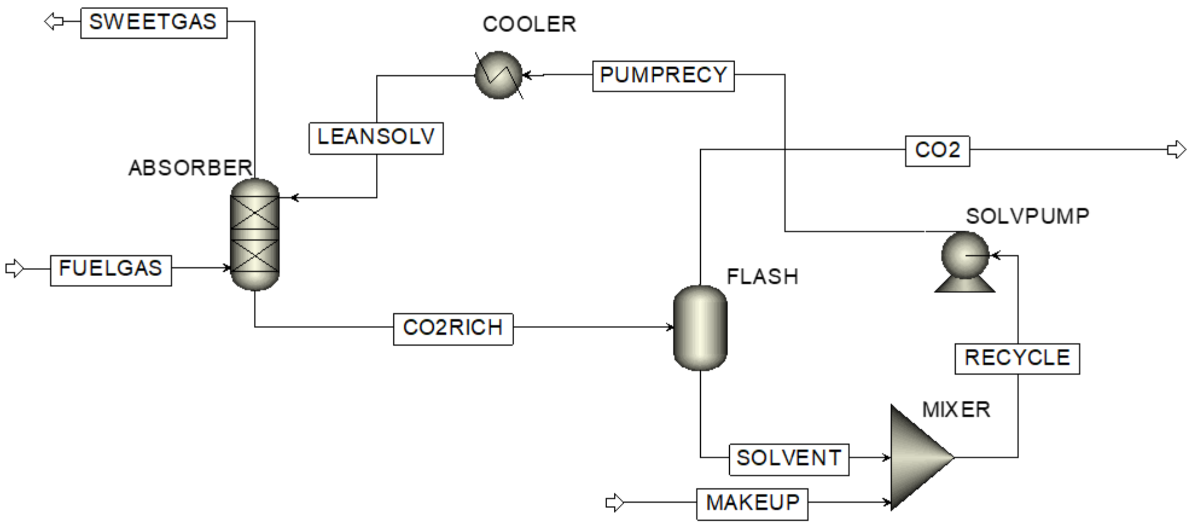
Solubility Results (Including Spot Check)

Gas component	Syngas partial pressure, MPa		Gas uptake, mol·L^{-1}	
	PEGDME	CASSH-1	**PEGDME**	**CASSH-1**
CO_2	2.66	2.74	**2.49 ± 0.03**	**2.40 ± 0.04**
N_2	1.29	1.18	**0.07 ± 0.03**	**0. 07 ± 0.01**
H_2	0.73	0.81	**0.01 ± 0. 01**	**0.03 ± 0.02**
CH_4	0.10	0.09	**0.01 ± 0.003**	**0.01 ± 0.002**
CO	0.07	0.04	**0.01 ± 0.004**	**0.01 ± 0.002**
H_2S	0.02	0.02	**0.02 ± 0.0002**	**0.02 ± 0. 0003**

Experimental Water Content After Flash After Test
PEGDME = 837 ppm CASSH-1 = 358 ppm

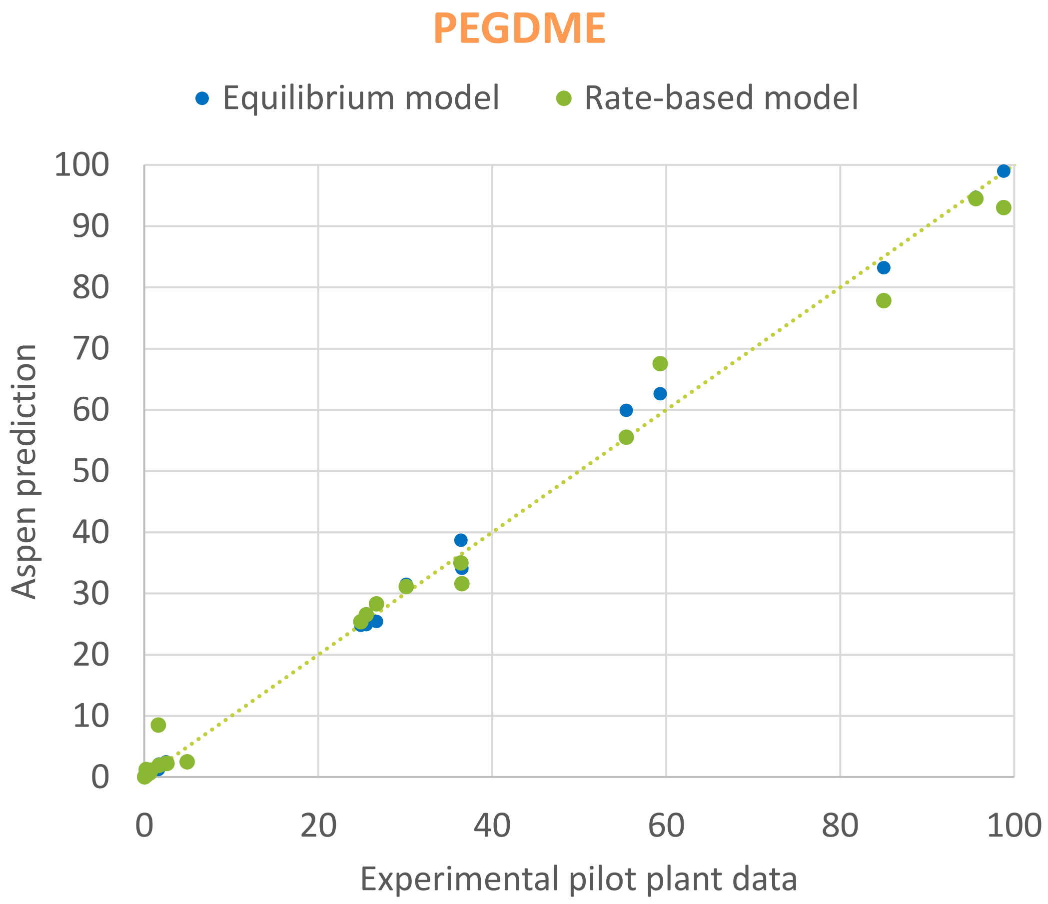
Aspen Plus Simulation of Pilot Plant

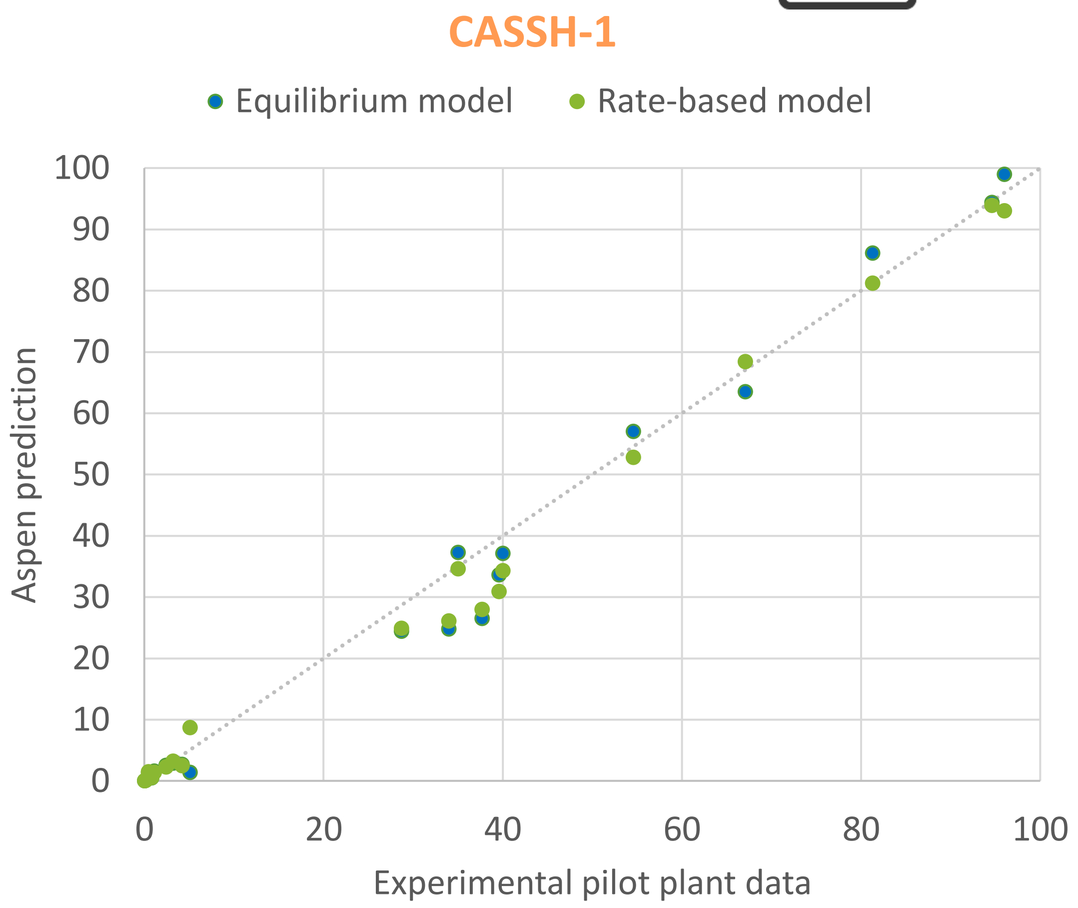
- VLE data was used to validate the thermodynamic properties predicted in Aspen Plus via the PC-SAFT Equation-of-State.
- The physical properties of gas species and solvents used were predicted via built-in models within Aspen Plus and validated using experimental data.
- Both rate-based and equilibrium models were used to predict absorber performance via the Aspen RadFrac block without a reboiler.



Parameter	PEGDME	CASSH-1
Solvent temperature, °C	25	25
Solvent flow rate, L/hr.	32.0	32.4
Absorber column pressure, MPa	4.86	4.86
Syngas flow rate, mol/h	145.3	149.6
Syngas temperature, °C	37.8	37.3
Syngas composition (dry), mol%		
H_2	15.3	16.64
N_2	27.0	25.93
CO	1.06	0.71
CO_2	54.5	54.9
CH_4	1.77	1.41
H_2S	0.34	0.41
Flash temperature, °C	66	66
Flash pressure, MPa	0.1	0.1
Packed bed height, m	3.2	3.2
Absorber diameter, m	0.0762	0.0762
Absorber packing material	5/8 ” IMTP15	5/8 ” IMTP15

Aspen Plus Process Simulation Results





Parameters include absorber temperature profile, sweet gas flow rate, acid gas flow rate, sweet gas composition, acid gas composition, CO_2 recovery & CO_2 uptake

Conclusions

- First pilot plant testing of hydrophobic physical solvents for CO_2 removal from coal-derived H_2-rich syngas at UND EERC
- Four physical solvents were tested under pre-combustion CO_2 capture conditions, both at bench scale and pilot plant scale:
  - (1) polyethylene glycol dimethyl ether, PEGDME (a hydrophilic physical solvent analog for the commercial process Selexol™ solvent),
  - (2) tributyl phosphate, TBP (a commercially available hydrophobic physical solvent),
  - (3) polyethylene glycol - poly(dimethylsiloxane), PEG-PDMS-3
  - (4) diethyl sebacate, known as CASSH-1 (a novel, computationally screened hydrophobic physical solvent developed by the National Energy Technology Laboratory, NETL).
- The hydrophobic solvents absorbed less water and showed comparable CO_2 absorption performance compared to the hydrophilic PEGDME, including at elevated absorption temperatures of up to 55°C and during long term operation.
- Pilot plant performance data for PEGDME & CASSH-1 compare well to process simulations which were developed by regressing bench-scale VLE data into Aspen Plus.
- Low viscosity, low vapor pressure hydrophobic solvents can be a promising option for lower cost carbon capture from high pressure gas applications.

Acknowledgements

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